

# Simulating the Adsorption Isotherms of Methane, Ethane, and Propane in the Zeolite Silicalite

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Computer simulations are used to simulate the adsorption isotherms of methane, ethane, and propane in the zeolite silicalite. Various zeolite–alkane models have been tested via a comparison with experimental heats of adsorption and Henry coefficients. These tests are used to improve the existing models. It is shown that the calculated adsorption isotherms agree well with the available experimental data. However, a definitive validation of the models is impeded by the large scatter of reported experimental data.

## I. Introduction

Zeolites are complex, crystalline inorganic materials which have a well defined microporous structure. Their high internal surface, internal acidity, and thermal stability are some of the unique properties that make them an important class of catalytic materials for petrochemical processes.<sup>1</sup>

In many practical applications of zeolites it is important to know the amount of material adsorbed inside their pores. Experimentally, it is difficult to obtain this type of information, in particular at reaction conditions. Computer simulations appear to be an attractive alternative to experimentation for determining the adsorption isotherms at conditions of interest. One of the first attempts to study the thermodynamic properties of a molecule adsorbed in a zeolite was made by Stroud *et al.*<sup>2</sup> Since this pioneer work, many articles have been published describing the use of molecular dynamics or Monte Carlo techniques to study the behavior of molecules adsorbed in zeolites.<sup>3–38</sup> A review of some of these simulation studies is given in ref 39.

In this paper we study the adsorption isotherms of methane, ethane, and propane in the zeolite silicalite. The technical details of the simulation techniques used are described in ref 40. A discussion of the models that are used in this work is given in section II, details of the simulations are described in section III, and the results are listed in sections IV–VI.

## II. Models

In this paper we focus on the adsorption of small alkanes in silicalite. Following Kiselev and co-workers,<sup>41</sup> we have assumed that the zeolite crystal is rigid. The silicalite structure is of the orthorhombic form with atomic positions taken from the X-ray diffraction.<sup>42</sup> In some studies the importance of a flexible zeolite structure is emphasized.<sup>16,25</sup> We expect that this framework flexibility can be of importance for the modeling of the diffusion of the molecules, since a flexible framework may reduce the diffusion barriers. Since these barriers correspond to positions in which the molecules have a relatively high energy and therefore do not contribute much to the equilibrium properties, it can be expected that the assumption of a rigid zeolite lattice is less severe for these properties. Important to note is that the adsorption of molecules may induce structural transitions of the zeolite lattice.<sup>43</sup> Since the techniques used in this work can also be used with a flexible framework—this will,

however, require significantly more CPU-time—it would be interesting to test the validity of the assumption of a rigid framework.

For the adsorption of alkanes it is reasonable to assume that the alkane–zeolite interactions are dominated by dispersive forces, which are described with a Lennard-Jones potential

$$U(r_{ij}) = \begin{cases} 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] & r_{ij} \leq R_c \\ 0 & r_{ij} > R_c \end{cases}$$

where  $r_{ij}$  is the distance between atoms  $i$  and  $j$ ,  $\epsilon$  is the energy parameter,  $\sigma$  is the size parameter, and  $R_c$  is the cutoff radius of the potential. The contribution of the atoms beyond the cutoff to the total energy is estimated using the usual tail corrections.<sup>44</sup> Since the size as well as the polarizability of the Si atoms are much smaller than those of the O atoms of the zeolite, it is assumed that the contributions of these Si atoms can be accounted for by using effective interactions with the O atoms.

The alkane molecules are modeled as united atoms; i.e., CH<sub>4</sub>, CH<sub>3</sub>, and CH<sub>2</sub> are considered a single interaction center. The interactions between these united atoms are also described with Lennard-Jones potentials. More details on the parameters for the various interactions are given in sections IV–VI.

Since in our model the zeolite is assumed to be a rigid crystal, the potential energy at a given point inside the zeolite can be calculated a priori. If this is done for points on a grid, the potential energy at an arbitrary point can be estimated from interpolation during the simulations.<sup>37</sup> With such an interpolation scheme a gain in CPU time of 1–2 orders of magnitude can be gained.

## III. Simulation Details

Most of the simulation studies investigate the energetics, siting, or diffusion of the adsorbed molecules, and only a few results on the simulation of isotherms have been reported. Soto and Myers<sup>3</sup> used grand canonical Monte Carlo simulations to determine the adsorption isotherm of krypton in the molecular sieve MS-13X. A similar technique was used by Wood and Rowlinson<sup>45</sup> to determine the adsorption isotherms of xenon and methane in zeolite X and Y, by Goodbody *et al.*<sup>15</sup> and by Theodorou and co-workers<sup>13,28</sup> for methane in silicalite, by Van Tassel *et al.*<sup>32,35</sup> for xenon, argon, and methane in zeolite NaA, and by Jameson *et al.*<sup>34</sup> for xenon in zeolite Na–A. Adsorption isotherms of mixtures were calculated by Karavias and Myers<sup>18</sup> for a mixtures of ethene–carbon dioxide as well as carbon

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dioxide-methane in zeolite X, by Maddox and Rowlinson<sup>30</sup> for a mixture of nitrogen and methane in zeolite Y, and by van Tassel *et al.*<sup>35</sup> for mixtures of noble gases and methane in the zeolite Na-A.

In this work we have used ordinary  $N,V,T$  simulations of one molecule adsorbed in silicalite to determine the Henry coefficients and heats of adsorption at zero loading. For ethane and propane we have used the configurational-bias Monte Carlo technique to determine the Henry coefficients; details on this technique in the context of simulations in zeolites can be found in ref 37. For the simulations of the adsorption isotherms we have used the grand canonical Monte Carlo method which is described in detail. More details on this technique can be found in ref 40. Below we give some of the details of the simulations that are specific for the various systems that have been studied. All simulations have been performed at a temperature of 298 K.

**A. Methane.** The  $N,V,T$  simulations were performed in cycles; each cycle consists of an attempt to displace a particle or an attempt to place the molecule at a new, randomly selected position. The probability to perform these two moves was set a priori such that on average 80% of the moves were attempts to displace a particle and 20% were attempts to move to a new position. In the displacement move the maximum displacement was given such a value that 50% of the moves were accepted. During the attempts to place the molecule at a random position, the "test-particle" energy was calculated from which the Henry coefficient was determined (see ref 47). A total simulation consisted of at least  $10^6$  cycles.

Also the grand canonical simulations were performed in cycles, each cycle consisting of an attempt to displace a particle and an attempt to add or remove a particle. The relative probability of these Monte Carlo moves was such that 90% of the moves were attempts to displace a particle and 10% of the moves were attempts to add or remove a particle. At higher loadings the number of attempts to add or remove a particle was increased to 30%. The simulations were started from the end configuration of a simulation at a lower chemical potential. We have allowed for at least  $10^4$  equilibrium cycles, and the subsequent production runs for at least  $10^4$  cycles at low loading and  $10^5$  cycles at high loadings. Tests for several loadings showed that this number of equilibrium cycles was sufficient to obtain equilibrium.

**B. Ethane.** In addition to the moves used for methane, in the  $N,V,T$  simulations of ethane an attempt was made to change the orientation of the ethane molecule by performing a rotation of the molecule. The maximum rotation was set to such a value that 50% of the moves were accepted. The relative probabilities of the attempts were such that 15% of the attempts were displacements, 15% rotations, and 60% of the moves attempts were to regrow the ethane molecule at a random position. For the latter move we have used the configurational-bias Monte Carlo scheme. In this scheme a molecule is grown atom by atom, and for each growing step we used three trial orientations.<sup>37,47</sup> A total simulation consisted of at least  $10^6$  cycles.

For the grand canonical Monte Carlo simulations the relative probabilities were 30% attempts to displace a particle, 30% attempts to change its orientation, and 50% attempts to add or remove a particle. Although for ethane it is possible to add or remove a particle using the conventional grand canonical Monte Carlo technique, we found it more efficient (a factor of 1.5–2) to use the combination of grand canonical Monte Carlo and the configurational-bias Monte Carlo technique as described in part I. In this scheme we used three trial orientations. A total

**TABLE 1: Experimental Heat of Adsorption ( $q_{st}$ ) of Methane, Ethane, and Propane in Silicalite/ZSM-5<sup>a</sup>**

| $T$ (K) | Si/Al ratio            | $-q_{st}$ (kJ/mol) | method | ref    |
|---------|------------------------|--------------------|--------|--------|
| Methane |                        |                    |        |        |
| 300     | $\infty$               | 18.1               | a      | 20, 63 |
| 300     | $\infty$ (Linde S-115) | 20.4               | a      | 51     |
| 300     | $\infty$               | 20.5               | g      | 54     |
| 300     | $\infty$               | 20.0               | a      | 52     |
| 300     | $\infty$               | 20.92              | a      | 50, 64 |
| 300     | 52                     | 28                 | a      | 48     |
| 423     | $\infty$               | 22.5               | g      | 65     |
| Ethane  |                        |                    |        |        |
| 293     | 34                     | 40.0               | a      | 66     |
| 293     | 130                    | 45                 | a      | 66     |
| 298     | $\infty$               | 30.5               | a      | 60     |
| 300     | $\infty$ (Linde S-115) | 32.8               | a      | 51     |
| 300     | $\infty$               | 29.9               | g      | 54     |
| 300     | $\infty$               | 31                 | a      | 67     |
| 301     | $\infty$               | 34                 | c      | 68     |
| 318     | 1230                   | 30                 | a      | 69     |
| 333     | 132                    | 30                 | a      | 59     |
| Propane |                        |                    |        |        |
| 300     | $\infty$               | 42.2               | ?      | 70     |
| 293     | 34                     | 44.5               | a      | 66     |
| 293     | 130                    | 46.5               | a      | 66     |
| 298     | $\infty$               | 38                 | a      | 60     |
| 300     | $\infty$               | 40.7               | g      | 54     |
| 325     | $\infty$ (Linde S-115) | 39.9               | a      | 51     |
| 318     | 1230                   | 40                 | a      | 69     |
| 318     | 135 (Na,H-ZSM5)        | 36.7               | a      | 69     |
| 333     | 132                    | 39                 | a      | 59     |
| 423     | $\infty$               | 36.5               | g      | 65     |

<sup>a</sup> The experimental methods are (a) adsorption isotherms, (c) calorimetry, and (g) gas chromatography.

simulation consisted of  $10^4$  equilibrium cycles and at least  $10^4$  production cycles.

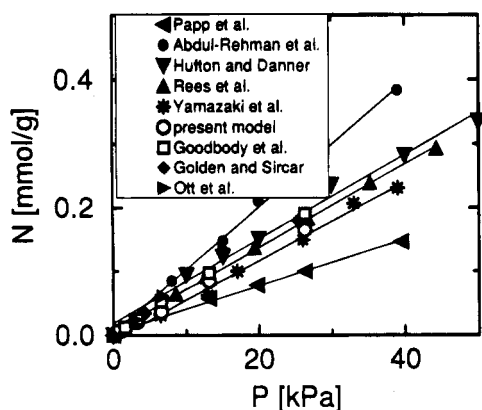
**C. Propane.** For the simulations of propane we used in addition to the moves described for ethane also a move in which part of the propane molecule is regrown; for this move the configurational-bias Monte Carlo scheme was used.<sup>46</sup> This move ensures that the different bond angles of propane are sampled efficiently (neither displacements nor rotations affect the bond angle of this molecule). The probabilities of the various moves in the  $N,V,T$  simulations were such that of the total number of moves 10% were attempts to displace, 10% attempts to rotate, 20% attempts to partly regrow the molecule, and 60% attempts to regrow the entire molecule at a random position. For the latter two moves we used four trial orientations. A total simulation consisted of at least  $10^6$  cycles.

For the grand canonical Monte Carlo simulations the relative probabilities were such that 25% of the attempts were a displacement of a particle, 25% a rotation, 10% partly regrowing the molecule, and 40% adding or removing a particle. For the latter two moves we used four trial orientations. A total simulation consisted of  $10^5$  equilibrium cycles and at least  $10^5$  production cycles.

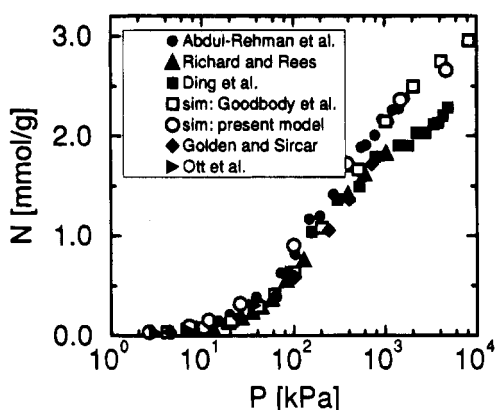
## IV. Methane

**A. Experiments.** Experimentally, the heat of adsorption of methane in silicalite/ZSM-5 has been determined using various methods. The results of these experiments are summarized in Table 1. The results reported by Papp *et al.*<sup>48</sup> deviate significantly from the other data. The reason for this deviation may be the low Si/Al ratio. Most other studies seem to agree on a value of about  $-20$  kJ/mol.

Adsorption isotherms of methane in silicalite have been determined by several groups.<sup>48–55</sup> The results of these



**Figure 1.** Experimental adsorption isotherms of methane in silicalite at low pressures (filled symbols). The lines show the fits from which the Henry coefficients have been determined, and the open symbols are the results from simulations at  $T = 298$  K.



**Figure 2.** Adsorption isotherms of methane in silicalite. The open symbols are the results of simulations at  $T = 298$  K. The closed symbols are experimental data.

experimental studies are compared in Figure 1 at low pressures and in Figure 2 at high pressures. The agreement between these studies is not as good as one would like. At low pressures the data from Hufton and Danner,<sup>54</sup> Yamazaki *et al.*,<sup>50</sup> Ott *et al.*,<sup>53</sup> Rees *et al.*,<sup>52</sup> and Golden and Sircar<sup>55</sup> are in very good agreement. The data from Abdul-Rehman *et al.*<sup>51</sup> and Papp *et al.*<sup>48</sup> appear to deviate significantly from the other results. A similar deviation of the result of Papp *et al.* for the heat of adsorption has been found. Abdul-Rehman *et al.* used Linde-S115, and in order to compare the data with silicalite, we have assumed that the 10% binder (silica) contained in this material does not contribute to the adsorption. This assumption seems not to hold.

From the available adsorption isotherms we have determined the Henry coefficients; we use  $K_H = 10.5$  mg/(g atm) as the experimental value for the Henry coefficient.<sup>56</sup> Also at high pressures (see Figure 2) the results from Abdul-Rehman *et al.* deviate from the results of Rees *et al.*<sup>52</sup> and Ding *et al.*<sup>49</sup> The latter two, however, agree very well. Ding *et al.*,<sup>49</sup> however, did not use silicalite, but Na-ZSM-5 and the presence of Na could affect the accessible volume for the adsorbed molecules significantly. The theoretical maximum loading of methane is estimated to be 3.75 mmol/g by Abdul-Rehman *et al.*,<sup>51</sup> while Rees *et al.*<sup>52</sup> estimated 2.7 mmol/g. Apparently, it is very difficult to determine the loading at high pressures. From the above we conclude that at low pressures accurate experimental data exist which can be used for a comparison with the simulation results. At high pressures the experimental data are not sufficiently accurate to be used for a quantitative comparison with the simulation results.

**TABLE 2: Comparison of the Parameters for the Zeolite–Methane, –Ethane, and –Propane Interactions**

| $\epsilon_{\text{CH}_4-\text{O}}$ (K) | $\sigma_{\text{CH}_4-\text{O}}$ (Å) | ref       |
|---------------------------------------|-------------------------------------|-----------|
| Methane                               |                                     |           |
| 133.3                                 | 3.214                               | 15, 28    |
| 169.3                                 | 3.187                               | 41        |
| 148.4                                 | 3.14                                | 20        |
| 97.5                                  | 3.885                               | 25, 26    |
| 90.79                                 | 3.694                               | this work |
| Ethane                                |                                     |           |
| 72.27                                 | 3.79                                | this work |
| Propane                               |                                     |           |
| 73.4                                  | 3.636                               | this work |

**TABLE 3: Comparison of the Monte Carlo Results for Methane in Silicalite for Various Models at  $T = 298$  K<sup>a</sup>**

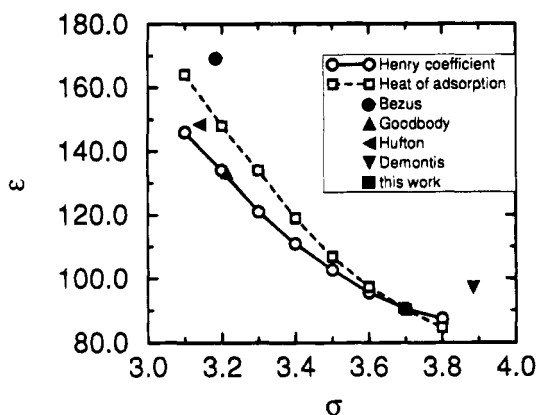
| simulation             | $-q_{\text{st}}$ (kJ/mol) | $\langle K_H \rangle$ [mg/(g atm)] | $\langle K_H \rangle_{\text{iso}}$ [mg/(g atm)] |
|------------------------|---------------------------|------------------------------------|---|
| Goodbody <i>et al.</i> | 18                        | 12.36                              |   |
| Goodbody (this work)   | 18.3 <sub>2</sub>         | 12.3 <sub>1</sub>                  | 11.9  |
| Bezus (this work)      | 22.3 <sub>1</sub>         | 53.9 <sub>1</sub>                  | 54.4  |
| Hufton (this work)     | 18.5 <sub>2</sub>         | 13.9 <sub>1</sub>                  | 14.1  |
| Demontis (this work)   | 24.1 <sub>1</sub>         | 30.8 <sub>1</sub>                  | 29.9  |
| present model          | 20.0 <sub>1</sub>         | 10.6 <sub>1</sub>                  |   |

<sup>a</sup>  $q_{\text{st}}$  is the isosteric heat of adsorption, and  $\langle K_H \rangle$ , the Henry coefficient. The subscript "iso" denotes that these results have been obtained from the adsorption isotherms. For comparison, the experimental heat of adsorption is  $-20$  kJ/mol and the experimental Henry coefficient is 10.5 mg/(g atm).

**B. Computer Simulations.** Molecular dynamics and Monte Carlo simulations have been used to study the behavior of methane in silicalite/ZSM-5,<sup>6,11–15,17,20,21,24–26,28,29</sup> faujasite,<sup>4,6,7,57</sup> Na-A,<sup>9,35</sup> mordenite,<sup>6,14</sup> and EU-1.<sup>14</sup> Monte Carlo simulations of mixtures of methane and other gases in zeolites are described in refs 18, 19, and 30. Of those who use a united atom model, the parameters are listed in Table 2. Comparison of the parameters used in the various studies shows that for the zeolite–methane interactions the values of the energy parameter  $\epsilon$  may differ by almost a factor of 2, and for the size parameter  $\sigma$  differences of 25% occur. The methane–methane interactions ( $\epsilon_{\text{CH}_4-\text{CH}_4} = 147.95$  K;  $\sigma_{\text{CH}_4-\text{CH}_4} = 3.73$  Å) are taken from the work of Verlet and Weis<sup>58</sup> and give a reasonable description of the vapor–liquid curve of methane. It is therefore interesting to make a detailed comparison of the various models to investigate how accurate the various sets of parameters describe the adsorption isotherms of methane in silicalite.

**1. Comparison with Goodbody *et al.*** Goodbody *et al.*<sup>15</sup> reported simulations of the adsorption isotherm of methane in silicalite. The data of Goodbody *et al.* have been reproduced by Maginn *et al.*<sup>28</sup> and are therefore ideal for testing our program. In Table 3 we compare the simulation results reported by Goodbody *et al.*<sup>15</sup> with the results obtained from our program. These simulations are  $N,V,T$  simulations of one adsorbed molecule. The agreement for the heat of adsorption and Henry coefficients is excellent. We have calculated the adsorption isotherms for a system with 4 and 8 unit cells. Our results are in excellent agreement with those of Goodbody *et al.* In addition we did not observe significant finite-size effects.

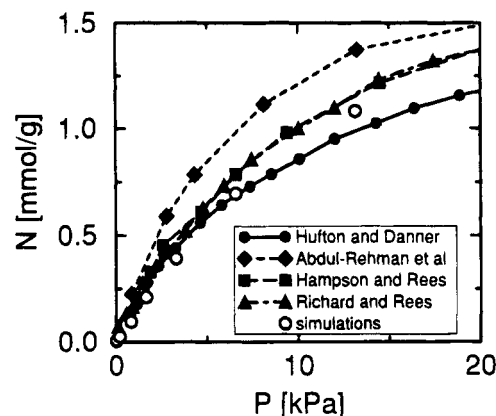
**2. Methane–Zeolite Interactions.** To test the various interaction parameters for the methane–zeolite interactions, we have calculated the Henry coefficient, heats of adsorption, and part of the adsorption isotherms for the various models. The results of these calculations are presented in Table 3. Table 3 shows that for most models the isosteric heats of adsorption are in good agreement with the experimental result, although the model used by Demontis *et al.*<sup>25</sup> seems to give a value which is somewhat large.



**Figure 3.** Optimum Lennard-Jones parameters for the heat of adsorption (dashed line with squares) and Henry coefficient (solid line with circles) of methane in silicalite. The crossing of the lines gives the parameters for which both the Henry coefficient and heat of adsorption agree with the experimental results. For comparison, the filled symbols are the parameters of the various models.

The results for the Henry coefficients show a larger variation. The model used by Bezus *et al.* predicts a Henry coefficient which is five times larger than the one predicted by the model of Goodbody *et al.*<sup>15</sup> A test of the consistency of the results is to calculate the Henry coefficient from the adsorption isotherms at low pressures and to compare these values with a direct calculation of the Henry coefficient using the test particle insertion method. The fitted Henry coefficients are given in Table 3. These Henry coefficients are in good agreement with the ones which have been calculated directly. The models of Demontis *et al.* and Bezus *et al.* predict a significantly higher adsorption than that observed experimentally. From the available models, the model of Goodbody *et al.*<sup>15</sup> agrees best with the experimental results. In addition we have found that although the models proposed by Bezus *et al.*<sup>41</sup> and Demontis *et al.*<sup>25</sup> give a good prediction of the heat of adsorption, the adsorption isotherm differs significantly from the experimental data. Apparently a good prediction of the heat of adsorption does not guarantee an accurate description of the adsorption isotherm as well; for the development of a model it is important to compare the Henry coefficients with experimental data as well.

Detailed comparison of the prediction of the model of Goodbody *et al.* with the experimental Henry coefficient and heat of adsorption shows that the heat of adsorption is slightly underestimated while the Henry coefficient is slightly overestimated. Note that these (small) differences occur because we use a different set of experimental data than was used by Goodbody *et al.*<sup>15</sup> To see whether the model can be improved, we have calculated the values of the parameters of the Lennard-Jones potential for the methane-zeolite interaction that reproduce the experimental Henry coefficient and heat of adsorption. The results of these simulations are shown in Figure 3. From the crossing of the two lines we can obtain the values for the Lennard-Jones parameters for which both the Henry coefficient and heat of adsorption are in agreement with the experimental data. The fact that there is such a point and that there is only one such point is an important result, since this suggests that there is a unique set of parameters which describes the properties of methane optimally. These values of the parameters are  $\epsilon = 90.79$  K and  $\sigma = 3.694$  Å. With these values the calculated Henry coefficient is 10.6 mg/(g atm) and the calculated heat of adsorption -20.0 kJ/mol. In Figure 3 we have also plotted the parameters used by the other groups. Comparison of our model with the model of Goodbody *et al.* shows that we have a significantly larger value for  $\sigma$ ; our value is close to the value



**Figure 4.** Comparison of the available experimental adsorption isotherms of ethane in silicalite at low pressures (filled symbols). The open symbols are the results from simulations at  $T = 298$  K.

used by Demontis *et al.* On the basis of the comparison of the model of Goodbody *et al.* with the experimental data, one would expect only a marginal modification of this model. The results of Figure 3 show, however, that our model deviates more than expected from the model of Goodbody *et al.* Note that "optimum" is defined as agreement with a particular set of experimental data. However, the specific experimental data used here are not unique; we made a "compilation" of these data and decided which values to use for our comparison. Our conclusions are therefore entirely dependent on the choices made here. We hope that more experiments will be performed to arrive at a unique experimental data set to eliminate this source of ambiguity.

**3. Adsorption Isotherms.** Figure 2 shows the adsorption isotherms at high pressures, where the size of the molecules dominates the energetics. Since the values of the size parameter for the zeolite-methane interactions are comparable (see Table 2), the results predicted by the model of Bezus *et al.* and Goodbody *et al.* converge to the same maximum loading. At pressures larger than 1000 kPa, the simulation results—as predicted by the model of Goodbody *et al.*—start to deviate from the experimental data of Rees *et al.*<sup>52</sup> and Ding *et al.*<sup>49</sup> Surprisingly, the simulation results are in good agreement with the data of Abdul-Rehman *et al.*<sup>51</sup> Since the experimental results at high pressures are not very reliable (see section IV.A), we can not draw too many conclusions from these results. In addition, in the simulations we assume silicalite to be a perfect crystal which is completely accessible to methane. Such ideal crystals are extremely difficult to make experimentally; one would therefore expect that experimental maximum loadings are systematically lower than the theoretical ones.

## V. Ethane

**A. Experimental Data.** The experimental data for the heat of adsorption of ethane in silicalite are collected in Table 1. The experimental data on pure silicalite converge to a value of -31 kJ/mol. Adsorption isotherms of ethane in silicalite have been published in refs 51, 54, 59, and 60. The data of these experimental studies are compared in Figures 4 and 5. At low coverage the data of Hufton and Danner,<sup>54,61</sup> Richard and Rees,<sup>59</sup> and Hampson and Rees<sup>60</sup> are in good agreement with each other. The data reported by Abdul-Rehman *et al.*<sup>51</sup> deviate slightly for similar reasons as those discussed for methane (see section IV.A). To determine the Henry coefficient, we have combined the low pressure data of Hufton and Danner,<sup>54,61</sup> Richard and Rees,<sup>59</sup> and Hampson and Rees.<sup>60</sup> Fitting all these data with equal weight yielded a Henry coefficient  $K_H = 330$  mg/(g atm).

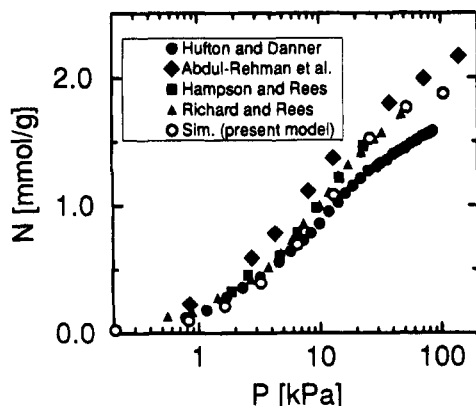


Figure 5. Comparison of experimental adsorption isotherms of ethane in silicalite with simulation data at  $T = 298$  K.

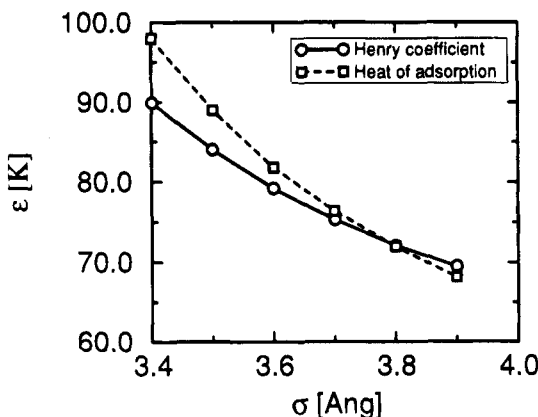


Figure 6. Optimum Lennard-Jones parameters of the heat of adsorption (squares) and Henry coefficient (circles) for ethane in silicalite. The crossing of the lines gives the parameters for which both the Henry coefficient and heat of adsorption agree with the experimental results.

This is consistent with the values  $K_H = 421$  mg/(g atm) reported by Hampson and Rees<sup>60</sup> and  $K_H = 460$  mg/(g atm) reported by Hufton and Danner.<sup>54</sup> For future comparison we use as experimental data for the heat of adsorption  $-31$  kJ/mol and for the Henry coefficient  $330$  mg/(g atm).

**B. Computer Simulations.** In contrast to the large number of simulations that have been published on the adsorption of methane in zeolites, there are only a few articles describing the adsorption of ethane. Titiloye *et al.*<sup>16</sup> used molecular mechanics to study the siting in silicalite. Catlow *et al.*<sup>17</sup> and Nowak *et al.*<sup>14</sup> studied the diffusion of ethane in silicalite. All these models use an all-atom representation. To our knowledge, united-atom models have not been used yet to study the adsorption of ethane in a zeolite. Before we consider the zeolite-ethane interaction, we first discuss the ethane model.

**1. Ethane Model.** The ethane model that is used in this work is based on the model developed by Jorgensen *et al.*<sup>62</sup> The bond length is fixed at  $1.536$  Å, and the nonbonded interactions are described with a Lennard-Jones potential with parameters  $\epsilon = 104.2$  K and  $\sigma = 3.775$  Å. The potential was truncated at  $13.8$  Å, and the usual tail corrections have been added.

**2. Zeolite-Ethane Interactions.** The simulations of methane demonstrated that, in order to describe the adsorption isotherms correctly, it is important to correctly predict both the heat of adsorption and the Henry coefficient at zero loading. To determine the optimum parameters for the  $\text{CH}_3$ -zeolite interactions for an ethane molecule, we used a similar procedure as that described for methane. Figure 6 shows the optimum parameters for the heat of adsorption and Henry coefficient; the intersection of the two lines ( $\epsilon = 72.27$  K and  $\sigma = 3.79$  Å)

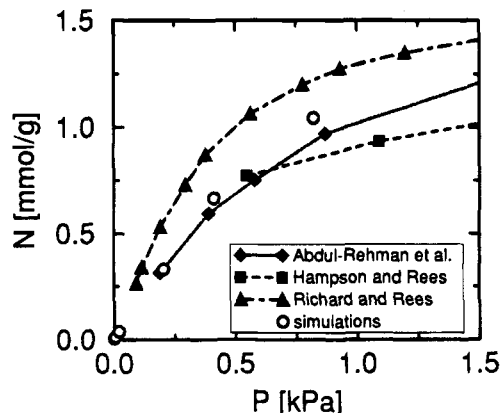


Figure 7. Comparison of the experimental adsorption isotherms of propane at low pressures.

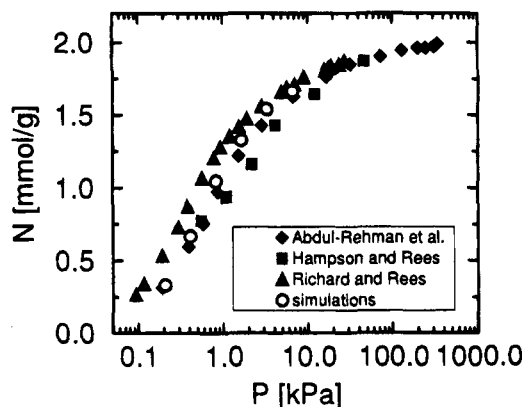


Figure 8. Comparison of experimental adsorption (filled symbols) isotherms of propane in silicalite with simulation data (open symbols) at  $T = 298$  K.

gives the model parameters. With this parameter set, we found a heat of adsorption of  $-31.1 \pm 0.1$  kJ/mol and a Henry coefficient of  $340 \pm 5$  mg/(g atm), in good agreement with the experimental values.

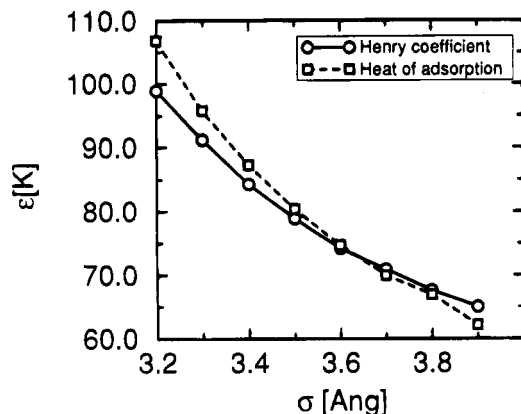
**3. Adsorption Isotherms.** In Figure 4 the simulation results are compared with the experimental data at low pressures. The simulations are in excellent agreement with the data from Richard and Rees<sup>59</sup> and Hampson and Rees.<sup>60</sup> Small deviations occur with the data of Hufton and Danner<sup>54,61</sup> and Abdul-Rehman *et al.*<sup>51</sup>

The adsorption isotherms at high pressures are shown in Figure 5. The simulation data differ significantly from the data of Hufton and Danner<sup>54,61</sup> but are in good agreement with the data of Richard and Rees,<sup>59</sup> Hampson and Rees,<sup>60</sup> and Abdul-Rehman *et al.*<sup>51</sup> The results presented in this section show that it is possible to model the experimental adsorption isotherms of ethane in silicalite accurately. Also for ethane it would be highly desirable that more experiments would be done since the experimental data show too much scatter to draw firm conclusions on the reliability of the models.

## VI. Propane

**A. Experiments.** The experimental data on the heat of adsorption of propane in silicalite are collected in Table 1. The experimental data on pure silicalite converge to a value of  $-40$  kJ/mol.

Adsorption isotherms of propane in silicalite have been published refs 51, 59, and 60. The data of these experimental studies are compared in Figures 7 and 8. At low coverage the data of Abdul-Rehman *et al.*<sup>51</sup> and Hampson and Rees<sup>60</sup> are in



**Figure 9.** Optimum Lennard-Jones parameters of the heat of adsorption (squares) and Henry coefficient (circles) for propane in silicalite. The crossing of the lines gives the parameters for which both the Henry coefficient and heat of adsorption agree with the experimental results.

good agreement with each other. The data of Richard and Rees<sup>59</sup> deviate slightly. Note that the isotherm of Richard and Rees was measured at a temperature of 291.5 K, while the other data are taken at 300 K. This temperature difference can explain the difference between the data sets. From the adsorption isotherms at low pressures (Figure 7) we have determined the following Henry coefficients: 4851 mg/(g atm) from the data of Abdul-Rehman *et al.*,<sup>51</sup> 6174 mg/(g atm) from the data of Hampson and Rees,<sup>60</sup> and 8379 mg/(g atm) from the data of Richard and Rees.<sup>59</sup> These values are in reasonable agreement with the extrapolated result 1014 mg/(g atm) obtained from chromatography by Hufton and Danner. For the determination of the propane-zeolite parameters we have used the (rounded) value of Hampson and Rees: 6200 mg/(g atm).

The experimental adsorption isotherms at high pressures are compared in Figure 8. All experimental data agree very well. This agreement is somewhat surprising since for methane and ethane systematic differences could be observed between the various data sets of the same sources.

**B. Simulations. 1. Propane Model.** We used the OPLS model of Jorgensen and co-workers<sup>62</sup> for the description of the nonbonded interactions of propane (Lennard-Jones parameters:  $\epsilon_{\text{CH}_3} = 88.06$  K,  $\epsilon_{\text{CH}_2} = 59.38$  K, and size parameter  $\sigma_{\text{CH}_3} = \sigma_{\text{CH}_2} = 3.87$  Å). Instead of a fixed bond angle, we used a bond-bending potential

$$U_{\text{bending}}(\theta) = \frac{1}{2}k_{\theta}(\theta - \theta_{\text{eq}})^2$$

with equilibrium angle  $\theta_{\text{eq}} = 112.4^\circ$  and  $k_{\theta} = 62\,500$  K.

**2. Zeolite-Propane Interactions.** Previous simulations of propane in silicalite of Nowak *et al.*<sup>14</sup> and Nicholas *et al.*<sup>29</sup> used all-atom representations of propane.

To determine the zeolite-propane interactions, we have used a similar procedure as for methane and ethane. We have assumed that the  $\text{CH}_3$  and  $\text{CH}_2$  groups have identical interactions. The optimum parameters for the heat of adsorption and Henry coefficient are shown in Figure 9; from this plot we obtain as parameters for the Lennard-Jones potential  $\epsilon = 73.4$  K and  $\sigma = 3.636$  Å. With these parameters the heat of adsorption is  $-39.9$  kJ/mol and the Henry coefficient 6406 mg/(g atm), which is in excellent agreement with experimental data.

**3. Adsorption Isotherms.** In Figure 7 the simulated adsorption isotherms of propane in silicalite are compared with experimental data at low pressures in Figure 7 and at high pressures in Figure 8. The agreement with experimental data is very good.

## VII. Concluding Remarks

In this paper the adsorption isotherms of methane, ethane, and propane in silicalite have been calculated using grand canonical Monte Carlo simulations. The zeolite-alkane models have been tested via a comparison of the experimental data for the Henry coefficients and heats of adsorption with the results obtained via simulations. It is shown that, among available methane-zeolite models, the model of Goodbody *et al.*<sup>15</sup> performed best. A new set of methane-zeolite parameters has been introduced which yields a better prediction of the experimental data than the model of Goodbody *et al.*<sup>15</sup> Also for ethane and propane new sets of parameters have been introduced which yield heats of adsorption, Henry coefficients, and adsorption isotherms that are in good agreement with experimental data.

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